1.0   Executive Summary

1.1   Introduction

1.1.1   Purpose and Goals of the Workshop

A workshop titled "Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal," was held on May 1 – 3, 2001, in Denver, Colorado. This workshop was sponsored and facilitated by the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) and Office of Solid Waste (OSW), Emergency Response. The purpose of the workshop was to achieve three goals:

1)   Examine the chemical fundamentals related to arsenic chemistry, speciation, and analytical issues;

2)   Examine the state of practice of existing and emerging technologies that treat and properly dispose of arsenic wastes; and

3)   Identify/characterize sources of arsenic.

The workshop was not designed to cover issues related to drinking water; rather, to focus on characterization of wastes, arsenic speciation, and treatment and disposal practices. To facilitate discussion of these issues, the workshop featured a series of speaker presentations at a plenary session, and moderated technical breakout sessions with additional speaker presentations and participant discussions. Topics for the 12 presentations during the plenary session included arsenic waste, chemistry, and treatment and disposal, as well as regulatory perspectives and information management. Technical breakout sessions looked more closely at arsenic chemistry, source identification, and treatment and disposal issues: presentations during these sessions were more specific to the session topics.

Presenters were from the EPA, U.S. Geological Survey (USGS), Government of Canada, state agencies, academia, federal laboratories, consulting firms, and technology developers. Presenters and other workshop participants were known for their knowledge and involvement in the field of arsenic waste and management.

This report provides a summary of the key issues pertaining to managing arsenic risks to the environment, followed by plenary speaker abstracts, breakout session discussion review and speaker abstracts, and lastly, appendices with the workshop agenda, attendees, and a selected arsenic publications bibliography. It is hoped that this information will be useful to anyone involved with managing arsenic issues, and will prompt additional work and research to resolve outstanding arsenic issues.

1.1.2   Background

It is well known that arsenic, especially the inorganic forms, is very toxic and is a carcinogen. The chemical nature of arsenic compounds, in particular their tendency to change valence states or chemical form under a wide range of pH and redox conditions, makes it difficult to assess their fate and mobility in the environment. Furthermore, case studies show that arsenic wastes that have been treated to U.S. regulatory standards are found to leach out of landfilled waste. A key issue for this workshop was, therefore, effective treatment and stabilization of arsenic wastes to minimize risk to health and the environment.

Arsenic wastes are generated from several industries such as mining and smelting operations. Currently in the U.S., arsenic contaminated wastes are subject to the Resource Conservation and Recovery Act (RCRA) land disposal restrictions and must be treated to meet Toxicity Characteristic Leaching Procedure (TCLP) limits. A RCRA hazardous waste is defined as a waste that produces an extract containing more than 100 times the maximum contaminant level (MCL) in drinking water for that specific chemical. The MCL for arsenic (50 ppb) was recently subjected to a critical review due to concerns about the association of long-term exposure to arsenic and serious health problems such as skin and internal cancers and cardiovascular and neurological effects. As a result of this review, a change in the arsenic MCL from 50 ppb to 10 ppb was promulgated. This new, lower MCL may have implications related to public perception of the risks associated with arsenic waste and contamination, treatment standards and effectiveness, and cost issues.

EPA funded several arsenic treatment studies throughout the 1990s and has research ongoing. Containing and minimizing arsenic contamination has been a priority for ORD. Projects have included mine waste technology, groundwater treatment using permeable reactive barrier (PRB) technology, transport and fate in sulfidic systems, and drinking water research including MCLs. OSW has been reviewing and re-evaluating solid waste treatment standards and evaluating the effectiveness of land disposal restrictions for management of arsenic waste.

Challenges and research opportunities for arsenic include:

- Arsenic chemistry and mobility at contaminated sites
- Risk assessment
- Public perception and trust in the science
- Long-term stability of treated arsenic wastes
- Stabilization design issues and organics interference
- Measurement of treatment effectiveness
- Disposal of residuals from drinking water plants

The following technical session discussion summaries speak to these challenges and other issues. Additional information is available in the speaker abstracts and detailed session discussions.

1.2   Summary of Breakout Session Discussions

1.2.1   Source Identification

In this technical session, researchers presented information about natural and anthropogenic (influence of man) sources of arsenic; characterizing and identifying arsenic in soils and sediments, coal deposits, and mining environments; and management of arsenic risk in marsh environments and the mining and wood treating industries. Arsenic data were presented from research at natural and industrial sites, and approaches for best communicating arsenic contamination and risk data to the public were discussed. Group discussions centered around three general questions:

1) What are the primary sources that contribute to arsenic releases to the environment?
2) What are the significant data gaps and information needs for characterizing and identifying arsenic sources and waste forms?
3) What are the important insights to be conveyed regarding the management of arsenic risks for decision makers?

Primary Sources. Arsenic in the environment occurs from both natural and anthropogenic sources. There has been an effort to differentiate between natural and anthropogenic impacts, particularly in areas where expansion and development is occurring and with limited water supplies. There is also a growing appreciation of the regional nature of residual arsenic contamination from agricultural and other anthropogenic sources such as copper and sodium-based arsenicals from herbicides and pesticides. Based on the information presented in this session, the primary natural sources of arsenic releases to the environment are: hot springs (geothermal), igneous rock (basalt), sedimentary rock (organic/inorganic clays, shale), metamorphic rock (slate), seawater, mineral deposits, and volcanoclastic materials/releases. The primary anthropogenic sources of arsenic releases to the environment include: historic mining sites, pesticide/herbicide use, combustion byproducts from burning fossil fuels, animal feeds/waste byproducts, historic wood preserving sites, medicinal uses, fertilizer use, landfill leachate, glass production, and tanneries.

Information Needs for Identifying and Characterizing Arsenic Sources and Wastes. Information is needed on anthropogenic and natural sources to identify parameters that affect treatment and to assess effects from anthropogenic constituents such as petroleum hydrocarbons from leaky pipelines. Site characterization techniques (e.g., oxidation, species concentration) and guidance are also needed for collecting and analyzing data. It may be possible to determine the source of the arsenic based on the presence of other source-specific anthropogenic chemicals/elements (tracers) or to understand the history of a pollution source by examining reservoir sediment samples, dendrochronological (tree wood) samples, and local records. Soil characterization information is needed that defines "natural" arsenic concentrations and conditions in different types of soils, and the impacts that arsenic introduction can have on different types of soil. More information is needed on arsenic mineralogy, bioavailability, leachability, and speciation, particularly for As(III) and As(V). Generic guidance is needed that can be used to help identify impacted media, characterize contamination, and assess potential impacts. Finally, information or techniques are needed which can be used to predict the future impacts of an arsenic release, including fundamental kinetics/thermodynamics.

Management of Arsenic Risks. Some of the primary conclusions from this session concerning management of arsenic risks are: 1) it is important to monitor arsenic releases and provide this information to the public; 2) the risk from an arsenic release needs to be well defined, and it is also important to differentiate real versus perceived risk; 3) during a risk characterization, the environmental effects of the arsenic release should be predicted; and 4) it is important to understand how to fix an arsenic contamination/release problem, and then monitor the performance of the selected corrective action.

There was a general consensus in this technical session that there is not enough information, either nationally or regionally, on background arsenic concentrations in soils. Since this information is very important, a national database/map is needed to address metals in soils. It is important, however, to identify criteria for collecting these samples, such as depth and the analytical method to use, before proceeding any further with this effort. There are also a number of sample libraries that could be used to develop the background information needed to assess human health and environmental impacts from arsenic. Efforts to set standards are complicated by difficulties determining the difference between "pristine" background concentrations and anthropogenic inputs after contamination has occurred. Although MCLs are used to protect human health, it is necessary to define how they relate to natural sources with high variability. Analytical methods must have low enough method detection limits (typically 10 to 20% of the MCL) to provide quantitative arsenic MCL results. The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic source identification issues.

1.2.2 Treatment and Disposal

There was a series of 11 presentations in the arsenic treatment and disposal breakout session. Speakers from Australia and Canada as well as the U.S. provided the arsenic issues and the challenges to assess the chemical fundamentals, as well as the treatment choices that are utilized to minimize arsenic's impact on the environment.

Group discussions centered around these general questions:

1) What are the long-term stability issues with regard to land disposal (i.e., on-site storage or landfills) of arsenic stabilized wastes?
2) How do current advances (i.e., molecular chemistry, leaching mechanisms) impact the areas of arsenic treatment and disposal?

The highest priority research needs in advancing arsenic treatment and disposal were also identified.

In 1996, the U.S. demand for arsenic in market products was estimated at 22,000 metric tons, making the U.S. the world's largest consumer. Most arsenic is used in wood preservatives, but significant use also occurs in agricultural chemicals, glass production, and metal alloys. These industrial practices and metals mining and smelting operations generate arsenic-bearing wastes. In 1998, the metal mining industry managed the most arsenic waste, over 617 million pounds or 96% of the total mass of arsenic waste managed. Gold mining accounted for about 93% of the arsenic mining wastes. Several federal cleanup programs, such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and RCRA, manage the remediation of contaminated sites that may contain arsenic. Most of the detailed data are available due to the cleanup of Superfund sites.

Long-term Stability. There are a number of test methods used to predict the performance of stabilized arsenic wastes, including the TCLP, Synthetic Precipitation Leaching Procedure (SPLP), and Multiple Extraction Procedure (MEP). In California, the Waste Extraction Test (WET) is used. There are issues with all of these test methods that make it difficult to predict the effects of time on the stability of treated wastes. Although EPA requires the use of TCLP for predicting the performance of stabilized arsenic wastes in a landfill, several concerns have been raised about the ability of this method to predict long-term stability. In addition, the other methods give different kinds of performance results and are not truly comparable between sites. Models that predict thermodynamic and kinetic variables can also be used to simulate long-term conditions and determine treated arsenic waste stability. The disposal environment of the waste must also be considered. For example, avoid placing wastes in saturated zones, and utilize capping materials to protect waste and minimize contact with leaching agents.

Current Advances. In research and development, advances in techniques and instrumentation have allowed for greater site investigation. For example, X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) often provide a better understanding of a material's microstructure. However, these advances have not yet transferred into field performance specifications. Researchers are investigating the toxicity of different arsenic forms such as As(III) and As(V). This research may result in developing different regulations for different species of arsenic.

Research Needs. Important research needs for arsenic treatment and disposal are: 1) improved understanding of long-term stability and protocols for simulating long-term conditions and performance, 2) improved understanding of waste chemistry, speciation, and biogeochemistry, 3) improved understanding of waste microstructure and mineralogy,

4) evaluation of biological processes (bacteria, fungi, plants) on arsenic mobilization, and 5) improved understanding of arsenic toxicity issues.

The change in the arsenic MCL from 50 ppb to 10 ppb could prompt EPA to change the required treatment standard to a value that is at or below the current TCLP regulatory level of 5 mg/L. If this is the case, then it is important to assess whether or not the current array of treatment options could achieve the potentially more stringent treatment requirements. However, treating high-concentration arsenic wastes is difficult and treatment costs associated with these technologies can be high. The key question is: are the high treatment costs justified by the incremental reduction in potential risk associated with arsenic in treated wastes? The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic waste treatment and disposal issues.

1.2.3 *Arsenic Chemistry*

The basis for the reliable prediction of arsenic mobility and treatment in subsurface systems is dependent on an adequate understanding of the chemical processes that control arsenic partitioning between the aqueous and solid phase. While significant effort has been expended to study the factors controlling arsenic fate and transport in environmental systems, the ability to predict arsenic mobility and exposure in a regional or ecosystem context is still inadequate. This inadequacy derives both from an incomplete compilation of the necessary chemical information and the application of inappropriate methods to collect these data. The goal of this session was thus to task a panel of experts to establish the current state of knowledge and to identify future areas of research and the most reliable pathways to fill existing data gaps.

Group discussions centered around three general questions:

1) Is our knowledge of arsenic speciation and transformation adequate to identify pathways and routes of mobility?
2) Are current collection, preservation, and analytical techniques sufficient for defining arsenic chemistry in natural and engineered systems?
3) Are existing leaching procedures adequate for characterization of arsenic-bearing waste materials?

Arsenic Mobility. Since arsenic is a redox-sensitive element, its chemical speciation is dependent on changes in system redox parameters that are driven by biotic and abiotic processes. The mobility of arsenic is tied to the cycling of major elements such as carbon, iron, and sulfur between the solution and solid phase in natural and engineered systems. While there is generally a sound phenomenological understanding of arsenic mobility, the ability to provide a quantitative assessment is limited. This limitation is due, in part, to the complexities of coupling chemical and hydrodynamic models in complex heterogeneous systems. This limitation is compounded by the existence of knowledge gaps, including: 1) coupling of arsenic chemical speciation to the cycling of redox-sensitive nutrients such as nitrogen, 2) knowledge of aqueous arsenic speciation in anoxic environments, 3) protocols for applying sorption models to describe arsenic solid phase partitioning, and 4) predictive tools and modeling approaches to describe the influence of microbial activity on arsenic mobility.

Analytical Tools. In general, existing analytical tools are satisfactory for quantification of arsenic chemistry in aqueous systems. However, attempts to apply these tools in a uniform manner for evaluation of all sample matrices are problematic. A matrix was developed to point out the strengths and limitations of the various analytical tools, and this information can be used as a guide for developing the most appropriate analytical protocol on a site- or case-specific basis. This limitation also applies to attempts to apply a single technique for preservation of arsenic chemistry prior to analysis. While there was agreement that filtration, acidification, and light exclusion are generally adequate for preservation of most aqueous samples, this approach must be validated and modified as required to achieve desired site-specific data quality objectives.

Waste Form Characterization. Leach tests have been developed to provide guidance as to the stability of solid waste forms prior to or following land disposal. Limitations have been identified for the application of existing test procedures for evaluation of arsenic stability (or mobilization potential) in waste solids. In particular, research indicates that the TCLP provides results that do not reflect the in-situ leaching behavior of arsenic for municipal solid waste. Design of leach tests should be governed both by the application of the test results and/or the in-situ chemistry anticipated for the disposal environment. For example, tests designed to assess differences in treatment process effectiveness may differ from those employed to assess the post-disposal leach potential of a solid waste form. Assessment of in-situ leach potential should focus on critical geochemical parameters that are characteristic for the disposal environment.

A re-occurring theme for all of the topics addressed in this session was that a degree of flexibility is required for application of the knowledge and tools employed to resolve arsenic waste problems. The complexity of arsenic chemistry is sufficiently high to preclude rigid protocols for site assessment and waste characterization. The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic waste chemistry issues.